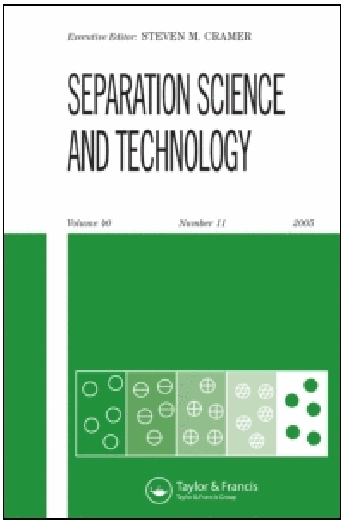

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The Development of a Simple Method for the Preparation of Reactor-Grade Zirconium

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Abstract

The separation of zirconium and hafnium by the fractional precipitation method has been extended by coprecipitation of their pyrophosphates. In the presence of sulfate ion, fractional precipitation of zirconium-hafnium pyrophosphates from a solution in 4 *N* HCl gives a good separation factor. Hafnium becomes concentrated in the precipitate. At a concentration of 0.7 to 0.8 g Zr/100 ml, optimum results were obtained with the addition of about 50 g ammonium sulfate/100 ml ($\lambda > 5$). The separation factor falls sharply at higher concentrations of zirconium. Moreover, it has been found that when precipitation of the host is done above 45%, the separation factor shows a declining trend. It was, therefore, not possible to prepare reactor-grade zirconium in a single stage. After several trials it was possible to find nearly optimum conditions for the separation. Finally, reactor-grade zirconium was obtained in three stages of precipitation with an yield of ~24%.

INTRODUCTION

Following the advent of power reactors, the importance of reactor-grade zirconium is now well known. Since the development of fractional crystallization method by Hevesy et al. (*1*) for the preparation of pure hafnium from zirconium minerals, several methods have been introduced for the separation of zirconium and hafnium, particularly with an eye to

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the preparation of reactor-grade zirconium. Excellent reviews on this work have been published (*2–4*).

In spite of recent interest in solvent extraction or ion-exchange methods of separation, the classical approach to separation based on fractional crystallization, fractional precipitation, fractional sublimation, etc. has not been entirely discarded. Thus the traditional method of fractional crystallization of potassium fluozirconate (or hafnate) is still in use for the preparation of reactor-grade zirconium on a commercial scale. A survey of the literature convinced us to pursue work in this line so that some efficient method for the preparation of reactor-grade zirconium might be suggested.

It will not be out of place to mention some of the important methods of separation based on fractional precipitation by complexing one of the constituents. Precipitation as phosphate (*5*) or ferrocyanate (*6*) gives a high separation factor. But because of certain disadvantages, these methods have lost commercial importance. It was of interest to study whether an efficient method based on fractional precipitation of Zr–Hf pyrophosphate could be developed.

It is well known that pyrophosphates of zirconium and hafnium are insoluble compounds. In the presence of a simple complexing agent such as sulfate, good separation factor may be obtained with fractional precipitation of zirconium and hafnium. Zirconium pyrophosphate precipitate coagulates nicely in acid medium and separation from solution becomes easy. Pyrophosphate has the further advantage of being easily converted into a soluble compound by boiling with sodium hydroxide solution, and thereby recycling becomes simple. Because of these points, fractional precipitation with sodium pyrophosphate formed the subject matter of our study.

EXPERIMENTAL

Zirconium oxychloride of spectrochemical purity was used as the starting material for the preparation of reactor-grade zirconium. It had a hafnium content of $\sim 2\%$. As tracer, ^{175,181}Hf supplied by BARC was used. The following procedure was adopted to ensure a thorough exchange between the tracer and the bulk of inactive hafnium in the starting material.

Tracer hafnium from the stock solution was added to a solution of inactive zirconium and hafnium in HCl. Zirconium and hafnium were precipitated from the solution by passing gaseous ammonia into it. The precipitate was washed with hot water and then dissolved in HCl. The whole operation was repeated, and a labeled stock solution of zirconium and hafnium in HCl acid was thus prepared.

All other reagents used in the experiment were of AnalaR grade. Sodium pyrophosphate used as the precipitating agent was prepared according to the method of Audrieth et al. (7). Disodium hydrogen orthophosphate was heated to 500°C for 5 hr. The product is reported to contain more than 98% $Na_4P_2O_7$.

In some preliminary investigations it was observed that in the presence of sulfate a good separation factor could be obtained in fractional precipitation with pyrophosphate. As the medium of study, 4 *N* HCl was used. In a 4 *N* HCl medium the coagulation of the precipitate is satisfactory. The operation also becomes easy in this acid concentration.

With the aim of finding the most favorable conditions for the preparation of reactor-grade zirconium, a large number of trials was made in the following manner.

In a 800-ml beaker (tall form) a solution of Zr and Hf in 4 *N* HCl was taken. The salts were labeled with $^{175,181}Hf$. A definite amount of ammonium sulfate was added to the solution which was warmed and stirred by a magnetic stirrer. The temperature of the solution was maintained at about 70 to 75°C. A measured volume of standard pyrophosphate solution was added drop by drop to the warm and agitated solution. The precipitate was obtained in an easily separable coagulated form. The precipitate was separated from the solution, and the necessary washing with water was done by centrifugation. The solution and washings could be used for further operations.

The pyrophosphates of Zr and Hf were boiled with NaOH for about 2 hr. The pyrophosphates decomposed and the phosphates went into solution, but zirconium and hafnium remained as precipitates. The precipitate was washed by centrifugation until it was free of phosphate. The zirconium-hafnium in the precipitate went easily into solution with HCl and thus could be used for further separations.

For measurement of the distribution of the activity between the precipitate and the solution, the solution with washings was made up to a standard volume. The counts of 10 ml of this solution were measured in a 20th Century liquid counter. From the remaining counts in the solution, the counts of uptake by the precipitate could be computed.

The zirconium and hafnium remaining in solution after precipitation were estimated as oxides through precipitation as hydroxides with ammonia.

The distribution factors (D and λ) were calculated from (*8*, *9*):

$$\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{solid}} = D\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{solution}} \tag{1}$$

$$\log\frac{\text{initial tracer}}{\text{tracer in solution}} = \lambda \log\frac{\text{initial carrier}}{\text{carrier in solution}} \tag{2}$$

DISCUSSION

It is a well-known fact that zirconium forms more stable complexes than hafnium. This fact has been utilized in a number of fractional precipitation methods. The present study is an extension in the same direction with pyrophosphate as the precipitating agent. In the presence of sulfate the separation factor is high, and this forms the basis of an interesting study on the preparation of zirconium that is almost free of hafnium.

In the separation of zirconium and hafnium by fractional precipitation, it was necessary to work out procedures which could give optimum yield and whose results would be satisfactorily reproducible. Several factors involved in this study might have some bearings on the results obtained. Experimental conditions were to be so standardized that the role of each important factor could be ascertained and ultimately an optimum condition found out.

We made a systematic survey of the effects of important independent variables on the coseparation process. Illustrative examples are presented in tabular forms. In order to determine the constancy of the distribution factors D and λ in this coseparation process, trials were made by varying the degree of precipitation while keeping the other variable nearly constant. Table 1 shows the results of this study. It was found that up to a certain limit (about 45% precipitation) the distribution pattern followed the heterogeneous law within the tolerance limit. There are wide fluctuations in the values of the homogeneous distribution factor (D) over the whole range of precipitation, which is not unexpected in the experimental conditions maintained. In subsequent comparisons, λ has been used. The degree of precipitation has been kept below 45%.

The following points should be noted about the headings of the columns in Tables 1 to 4. By percentage of hafnium, in column 3 or 4, is meant the percentage of Hf calculated on the basis of total Hf + total Zr (by weight) = 100. The hafnium content of the starting solutions as reported by Johnson Matthey & Co was about 2%. Removal of hafnium in each stage of separation was estimated from the measurement of radioactivity left in

TABLE 1

The Study of the Constancy of the Distribution Factor with Variation in the Percentage of Zr Precipitated[a]

	Starting aqueous solution								
Experiment no.	Grams of $(Zr + Hf)$/100 ml	% Hf	Volume (ml)	Acidity in HCl (N)	Grams of ammonium sulfate/100 ml	% of Zr pptd	% of Hf uptake	λ	D
1	0.878	2.0	100	4	60.5	9.88	40.67	5.0020	6.2526
2	0.892	2.0	100	4	62.5	22.75	75.85	5.5107	10.6648
3	0.884	2.0	100	4	62.0	28.35	84.25	5.5435	13.5192
4	0.920	2.0	100	4	65.2	37.74	90.11	4.8845	15.0308
5	0.933	2.0	100	4	65.2	39.65	93.72	5.4801	22.7146
6	0.924	2.0	100	4	65.8	43.27	92.63	4.5995	16.4782
7	0.915	2.0	100	4	64.9	58.60	94.92	3.3782	13.2006
8	0.926	2.0	100	4	65.5	70.45	97.35	2.9782	15.4087
9	0.928	2.0	100	4	67.2	79.59	97.20	2.2499	8.9021

[a] Temperature maintained during precipitation was 70 to 75°C. Distribution factors assume a diminishing trend as a higher percentage of zirconium is precipitated.

the solution. Zirconium (and hafnium when necessary) in the solution was estimated gravimetrically. From the knowledge of initial and final amounts of zirconium and hafnium and the uptake of hafnium from radioactive measurements, the Zr:Hf (by weight) in the solution after precipitation has been computed. In a multistage process the percentage of precipitation of Zr and Hf in every stage has been expressed in terms of the total Zr and Hf in the starting aqueous solution.

The presence of sulfate ion in aqueous solution has an important influence on the separation factor. As can be seen from Table 2, very little separation can be achieved in the fractional precipitation of Zr–Hf pyrophosphate from an acidified aqueous solution without the addition of ammonium sulfate. The separation factor increases with an increase of sulfate concentration in the solution. For a Zr–Hf concentration of 0.7 to 1.0 g/100 ml in solution, the optimum result was obtained at an ammonium sulfate concentration of about 50 g/100 ml (Table 2).

For the maximum possible yield of zirconium free of hafnium, the amount of zirconium in a definite volume of solution should be increased as far as possible, provided the separation factor remains reasonably high. Studies were made on the effect of an increasing concentration of zirconium on the separation factor while keeping the other variables nearly constant. The results are presented in Table 3. The separation factor falls sharply after a zirconium concentration of 1.0 g/100 ml is reached. In subsequent trials the zirconium concentration was kept in a range of 0.8 to 1.0 g/100 ml. The question naturally arises as to the cause of this decline. It is probably due to the fact that the concentrated zirconium complex exercises some stabilizing influence on the corresponding hafnium complex. It is true that the ammonium sulfate that was added in the solution could not be increased in the same proportion as that in zirconium. However, even in comparable cases (see experiment 2, Table 2, and experiment 4, Table 3), the tendency for the separation factor to decline is quite evident.

The concentration of acid in the solution does not have any appreciable influence on the coseparation factor. As a medium of study, 4 *N* HCl was chosen because of certain favorable factors, e.g., the high solubility of zirconium oxychloride at this concentration as well as the satisfactory coagulation of the precipitate. Slight preheating of the solution was also necessary. At room temperature the precipitate was obtained in a gelatinous form, and separation is a difficult job.

In the application of this procedure for separation, our goal was to obtain the greatest possible yield of zirconium containing less than 200 ppm hafnium. Table 1 shows the extent of separation that can be achieved

TABLE 2

Effect of Sulfate Concentration on the Coseparation Factor in the Fractional Precipitation of Zr–Hf Pyrophosphates[a]

	Starting aqueous solution							
Experiment no.	Grams of (Zr + Hf)/100 ml	% Hf	Volume (ml)	Acidity in HCl (*N*)	Grams of ammonium sulfate/100 ml	% Zr pptd	% Hf uptake	λ
1	0.625	2.0	100	4	—	31.9	36.03	1.1631
2	0.672	2.0	100	4	16.70	22.75	66.88	4.2806
3	0.714	2.0	100	4	33.40	22.50	71.35	4.8909
4	0.705	2.0	100	4	50.10	22.65	75.64	5.4955
5	0.737	2.0	100	4	66.80	22.70	75.85	5.5196
6	0.724	2.0	100	4	75.40	27.16	82.17	5.4379

[a] Temperature maintained during precipitation was 70 to 75 °C. The optimum result is obtained for the addition of about 50 g of ammonium sulfate/100 ml solution.

TABLE 3

Effect of Varying Concentration of Zirconium in Aqueous Solution on Coseparation Factor[a]

Experiment no.	Starting aqueous solution: Grams of (Zr + Hf)/100 ml	% Hf	Volume (ml)	Acidity in HCl (*N*)	Grams of ammonium sulfate/100 ml	% Zr pptd	% Hf uptake	λ
1	0.672	2.0	100	4	55.2	28.35	84.25	5.5435
2	1.014	2.0	100	4	65.7	39.25	94.10	5.6818
3	1.252	2.0	100	4	70.6	37.07	86.86	4.0328
4	2.004	2.0	100	4	75.2	54.13	80.10	2.0711
5	2.718	2.0	100	4	80.7	59.84	76.58	1.5911

[a] Temperature maintained during precipitation was 70 to 75 °C. After a zirconium concentration of about 10 g/l, λ values begin to decrease sharply.

for different degrees of zirconium precipitation. As the separation factor begins to decline after precipitation of about 45% Zr, the necessary degree of separation of hafnium for reactor-grade zirconium could not be obtained in a single stage by precipitating a calculated amount of zirconium from solution.

It was, therefore, necessary to make an empirical selection of conditions so that optimum results could be obtained. It has been our experience that if the precipitate is removed from the solution after a certain degree of precipitation, and then further precipitation is done from the cleared solution, some improvement in separation is achieved. Perhaps, in the presence of a preponderant amount of zirconium ions in the solution, the accumulated precipitate adsorbs zirconium from the solution and thus decreases the separation factor. Therefore, introduction of the next stage of separation at a point where the separation factor had begun to decline sharply became advantageous for the overall scheme.

There are always a number of possibilities as to how one can put together the individual separation stages into a multistage fractionating scheme. We first made a thorough study of the first stage of precipitation by varying the degree of precipitation up to ~80%. Since it was not possible to prepare reactor-grade zirconium in a single stage even at ~80%, we tried two-stage separation procedures. Further addition of ammonium sulfate did not have any effect on the separation factor in the second stage. In an attempt to create a proper combination of the two stages, several combinations were tried for a total precipitation of from 40 to 80%. After a total precipitation of 60%, the separation factor started to decrease quite sharply. In spite of the fact that better separation was achieved in a two-stage separation process than in a single one, the required reactor-grade product was not obtained even after 80% precipitation.

So a further stage was necessary. Here again there was the question of combining the three stages in such a way as to gain the maximum yield of the required product. In the two-stage trials it was found that the separation factor remained at its peak value up to a total precipitation of about 45%, and that it was quite gainful up to a total precipitation of about 60%. So in the first two stages the degree of precipitation was varied from 45 to 60%, and the third stage had the limitation that the total precipitation had to remain below 80%. Three typical cases are presented in Table 4. In case 1, the hafnium content of the final product is slightly above that permissible for reactor-grade zirconium, and the yield of zirconium is ~33%. In cases 2 and 3, reactor-grade zirconium is obtained in about 24% yield. Provided the degree of precipitation in the first two stages was not less than

TABLE 4

Preparation of Reactor-Grade Zirconium in a Three-Stage Separation Process[a]

		Starting aqueous solution								
Trial no.	Stage no.	Grams of (Zr + Hf)/ 100 ml	Hf	Volume (ml)	Grams of ammonium sulfate/100 ml	% total Zr pptd	% total Hf uptake	λ	Zr/liter in the remaining solution	remaining Zr:Hf in the solution
1	1st	0.837	2.0%	100	55.8	32.76	85.76	5.0231	5.68	10^6:4198
	2nd	0.568	4198 ppm	100	55.8	17.66	11.23	5.1526	4.20	10^6:1200
	3rd	0.420	1200 ppm	100	55.8	17.48	2.49	4.0972	2.71	10^6:318
2	1st	1.014	2.0%	100	60.4	33.54	87.47	5.0822	6.74	10^6:3770
	2nd	0.674	3770 ppm	100	60.4	16.92	10.09	5.5681	5.02	10^6:985
	3rd	0.502	985 ppm	100	60.4	25.76	2.23	3.3423	2.41	10^6:176
3	1st	0.978	2.0%	100	60.5	37.43	89.87	4.8840	6.12	10^6:3237
	2nd	0.612	3237 ppm	100	60.5	21.29	8.44	4.3062	4.04	10^6:409
	3rd	0.404	409 ppm	100	60.5	17.14	1.48	3.8871	2.36	10^6:174

[a] Temperature maintained at 70 to 75 °C. Acidity of the solution was 4 *N* HCl. The yield of reactor-grade zirconium in Trials 2 and 3 was 23.78 and 24.14%, respectively. The yield of zirconium in Trial 1 was 32.69%, but the product contained slightly more hafnium than reactor-grade zirconium.

40%, the distribution among the three stages did not make much difference.

The zirconium (and hafnium) in the precipitate can be reused in separation cycle, and the yield of reactor-grade zirconium may be substantially increased. It has been mentioned that one specific advantage of this method is that the precipitate can be easily decomposed by boiling with NaOH solution, with the result that the zirconium and hafnium in solution can be used again. To clarify this point, some concrete examples from our experiments may be cited. The precipitates of zirconium at the 2nd and 3rd stages in trial 3 of Table 4 have lower hafnium contents than the starting materials, and they may be used in an appropriate way in the 2nd or 3rd stage of separation. Thus, if zirconium in the precipitates at stages 2 and 3 in this case is placed into solution and thoroughly mixed, the zirconium in the solution will have a hafnium content very close to that of the starting solution at the 2nd stage of precipitation. Further studies are required to determine the procedures for how these precipitates can best be utilized.

This study, therefore, enabled us to device a scheme of preparing reactor-grade zirconium. However, some analytical problems need further study for proper explanation. In this connection a few words about the composition of zirconium pyrophosphate should be presented. In the estimation of zirconium in the microscale, it was reported (*10*, *11*) that precipitation took place according to

$$Zr + Na_4P_2O_7 \rightarrow ZrP_2O_7$$

It was observed in our study in the macroscale that the zirconium actually precipitated by the addition of a certain amount of pyrophosphate did not correspond exactly to the above equation. So the pyrophosphate precipitate obtained in our experimental conditions was separated, washed, and the constituents brought into solution with NaOH. The zirconium and phosphorous were then estimated. The atomic ratio of Zr:P turned out to be about 1:1.5; had the precipitated material been pure ZrP_2O_7, this ratio would have been 1:2. In anticipation that the precipitate might be a mixture of the two compounds ZrP_2O_7 and $(ZrO)_2P_2O_7$, we performed a series of experiments under two sets of conditions which favored the formation of one of the two compounds. In one set, dilute pyrophosphate solution was added to a concentrated zirconium solution. It was expected that $(ZrO)_2P_2O_7$ would be produced under this condition. In the other set, dilute zirconium solution was added to concentrated pyrophosphate solution, and this should favor the formation of ZrP_2O_7. Although under a particular set of conditions the composition of the precipitate came closer to being that of the expected compound, it was never found to be identical with a pure compound. Probably some amount of another variety was always formed.

Further study is required to explain all aspects of the process. However, since the results are reproducible, it has been possible for us to suggest nearly optimum conditions for the preparation of reactor-grade zirconium. It should be mentioned that various methods have been proposed and are being practised in various laboratories in connection with this interesting process of separation. We are also trying to develop a new method which should be simple and less costly. The favorable points of the method are its high separation factor ($\lambda > 5$), which is comparable to other successful ones such as TBP or ion-exchange methods; the simplicity of the technique involved; and the use of cheap chemicals. The disadvantage of the method is that by nature it is a batch process and cannot be developed into a countercurrent continuous process. From our data and findings it can be said that the method that we have developed can be set up as a very easy method for the preparation of reactor-grade zirconium on a laboratory scale.

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